

M.Sc.(Chem.) Semester - 4 (CBCS) Examination
May/June-2021 (NEW COURSE)
Modern Spectroscopy (Elective)

Time: 1:30 Hours

Marks: 42

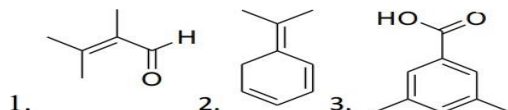
Instructions:

1. Figures to the right indicate marks.
2. There are five questions in the question paper.
3. Answer any three of the following questions.

Que-1(A) Discuss Bathochromic Shift and Hypsochromic Shift in UV spectroscopy. (04)

Que-1(B) **Answer any two questions out of three.** (10)

1. Describe types of electronic transitions in UV-visible range and discuss its energy order.
2. State and Derive Lambert-Beer's Law.
3. Calculate the wavelength ($\lambda_{\max}$) for following compounds:



Que-2(A) Discuss any two non-fundamental modes of vibration observed in IR spectroscopy. (04)

Que-2(B) **Answer any two questions out of three.** (10)

1. Discuss solid sample handling techniques in IR spectroscopy.
2. Explain instrumentation of IR spectroscopy with schematic diagram.
3. Explain stretching and bending modes of vibration in IR spectroscopy.

Que-3(A) **Define the following terms:** (04)

1. Base peak
2. Parent ion peak
3. Metastable ion peak
4. Rearrangement ion peak

Que-3(B) **Answer any two questions out of three.** (10)

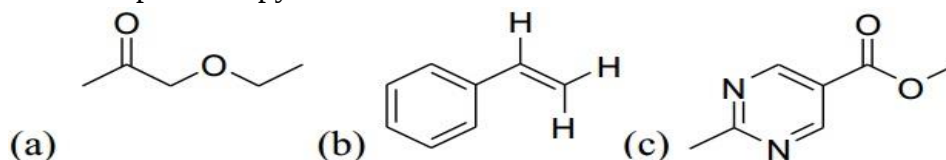
1. Discuss instrumentation of Mass spectroscopy with schematic diagram.
2. Explain McLafferty rearrangement with examples.
3. Discuss homolytic cleavage and heterolytic cleavage with example.

Que-4(A) **Answer the following questions** (04)

1. Give full form of COSY, NOESY, HSQC and HMBC.
2. Which types of nuclei are NMR active?

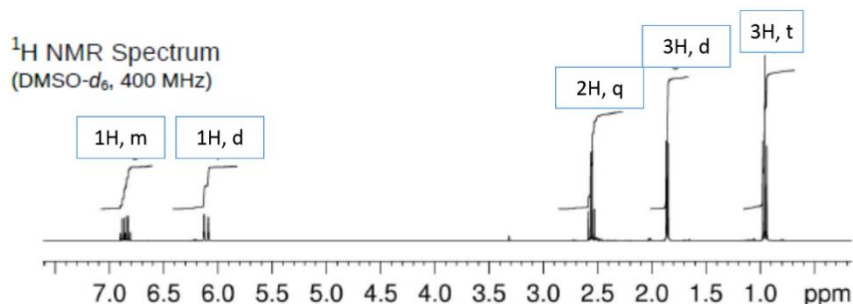
Que-4(B) **Answer any two questions out of three.** (10)

1. Predict the number of signals and its multiplicity for following compounds in NMR spectroscopy:



2. What is Magnetic Anisotropy? Explain with example.

3. Deduce the structure of the compound from the following ^1H NMR spectrum:
M.F: $\text{C}_6\text{H}_{10}\text{O}$

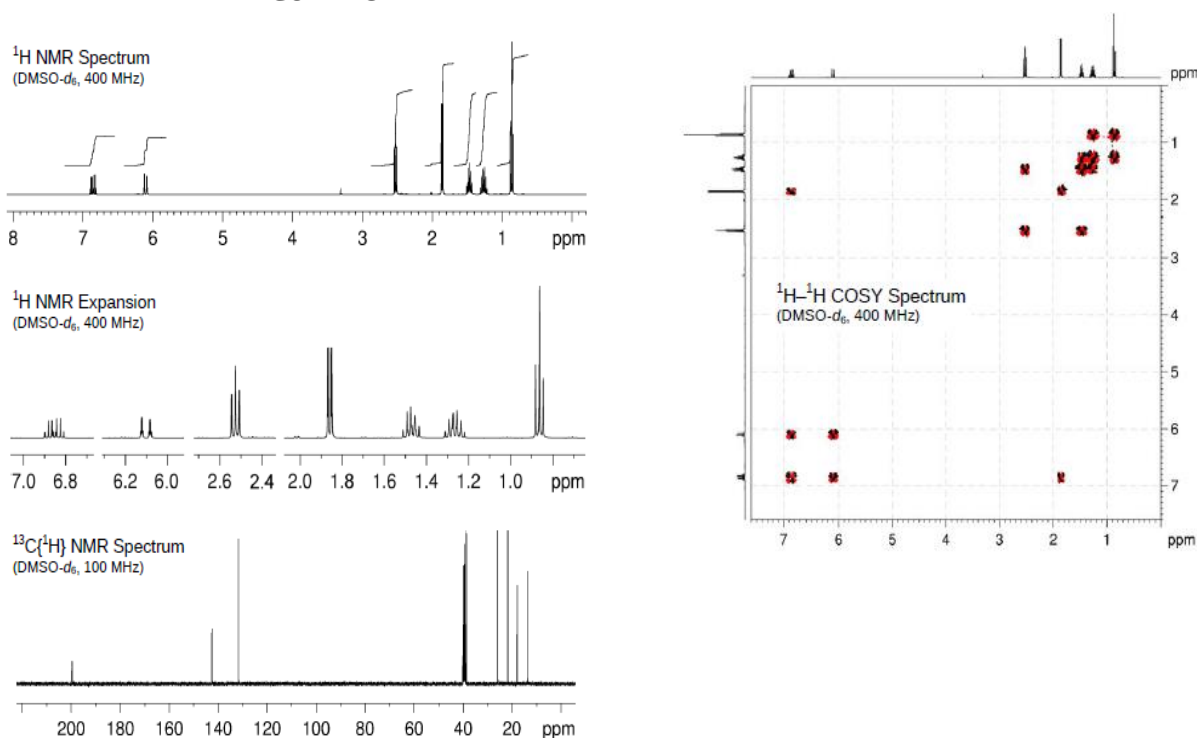


Que-5(A) Calculate the chemical shift value of carbon of following compounds: (04)

- (i) 4-nitrobenzoic acid (ii) p-xylene (iii) 3-pentanol

Que-5(B) Answer any two questions out of three. (10)

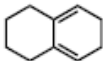
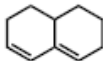
- Give the number of signals and their multiplicity in the proton-noise decoupled and off-resonance decoupled ^{13}C NMR spectra of the following compounds:
(a) Isopropyl benzene (b) 1-Pentene (c) Chlorobenzene
(d) p-Cresol (e) Benzaldehyde
- Deduce the structure of compound from the given analytical data.
MW: 158 g/mol, Elements: C-60.8%, H-8.8%.
IR: 2910, 1830, 1750, 1410, 1385, 1365, 1225, 1050 cm^{-1}
PMR: a/septate/2H/2.73 δ ppm, b/doublet/12H/1.20 δ ppm.
CMR (Proton noise decoupled): 3 Signals (δ ppm: 18.8, 35.6 and 173.2)
- Deduce the structure of compound from the given spectral data and interpret correlation peak in 2D NMR and assign protons.
MF $\text{C}_8\text{H}_{14}\text{O}$



Standard Data Sheet for UV spectroscopy

UV Spectroscopy

Woodward Fieser Rules for Dienes

			
	<i>s-trans</i>	homoannular (cisoid)	heteroannular (transoid)
base values:	217 nm	253 nm	214 nm

Increments:

For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
For each alkyl group or Ring Residue	+ 5 nm
For each homodiene component	+ 39 nm
For each of the following groups:	
- OR	+ 6 nm
- O(C=O)R	+ 0 nm
- Cl	+ 6 nm
- Br	+ 6 nm
- SR	+ 30 nm
- NR ₂	+ 60 nm
- Ph	+ 60 nm

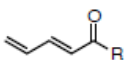
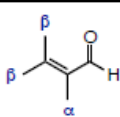
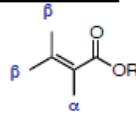
not affected by solvent

Where both types of cyclic dienes are present, the base with the longer λ_{max} is used.

UV Spectroscopy

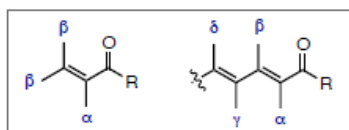
Woodward Fieser Rules for Enones and other Conjugated Carbonyl System

Solvent Correction	nm
H ₂ O	- 8
EtOH	0
CHCl ₃	+ 1
Dioxane	+ 5
Et ₂ O	+ 7
Hydrocarbon	+ 11

						
	acyclic enone	6-membered ring enone	5-membered ring enone	acyclic dienone	aldehydes	carboxylic acid or ester
base values:	215 nm	215 nm	202 nm	245 nm	208 nm	195 nm

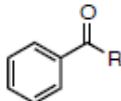
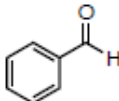
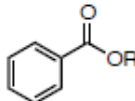
Increments:

		α	β	γ	δ and higher
For each additional conjugated double bond		+ 30 nm			
For each exocyclic double bond		+ 5 nm			
For each homodiene component		+ 39 nm			
For each alkyl group		+ 10 nm	+ 12 nm	+ 18 nm	+ 18 nm
For each of the following groups:					
- OH		+ 35 nm	+ 30 nm		+ 50 nm
- OR		+ 35 nm	+ 30 nm	+ 17 nm	+ 31 nm
- O(C=O)R		+ 6 nm	+ 6 nm		+ 6 nm
- Cl		+ 15 nm	+ 12 nm		
- Br		+ 25 nm	+ 30 nm		
- SR		+ 30 nm	+ 85 nm		
- NR ₂		+ 60 nm	+ 95 nm		



UV Spectroscopy

Woodward Fieser Rules for Benzoyl Derivatives

				
	aryl ketones (R = alkyl)	benzaldehydes	benzoic acids and esters	
base values:	246 nm	250 nm	230 nm	
Increments:		ortho	meta	para
For each alkyl group or RR		+ 3 nm	+ 3 nm	+ 10 nm for RR +7 nm
For each OH or OR (R = alkyl)		+ 7 nm	+ 7 nm	+ 25 nm
For each O [⊖]		+ 11 nm	+ 20 nm	+ 78 nm
For each of the following groups:				
- Cl		+ 0 nm	+ 0 nm	+ 10 nm
- Br		+ 2 nm	+ 2 nm	+ 15 nm
- NH ₂		+ 13 nm	+ 13 nm	+ 58 nm
- NH(C=O)CH ₃		+ 20 nm	+ 20 nm	+ 45 nm
- NHCH ₃				+ 73 nm
- N(CH ₃) ₂		+ 20 nm	+ 20 nm	+ 85 nm

Standard Data Sheet for IR spectroscopy

CHARACTERISTIC INFRARED ABSORPTION BANDS OF FUNCTIONAL GROUPS

Class of Compounds	Absorption, cm ⁻¹	Intensity	Assignment	Class of Compounds	Absorption, cm ⁻¹	Intensity	Assignment
Alkanes and Alkyls	2850-3000 1450-1470 1370-1390 1365 + 1395 (two bands) 715-725	s s m m w	C-H stretch C-H bend CH ₃ C-H bend -CH(CH ₃) ₂ or -(CH ₃) ₃ bend -(CH ₂) _n bend	Carboxylic Acids	2500-3500 R-C(O)-OH 1710-1715 C=C-C(O)-OH or Ar-C(O)-OH 1680-1710	s, broad s, broad s	O-H stretch C=O stretch C=O stretch
Alkenes	3020-3140 1640-1670 RCH=CH ₂ 910 + 990 (two bands) RR'C=CH ₂ 885-895 <i>cis</i> -RCH=CHR' 665-730 <i>trans</i> -RCH=CHR' 960-980 RCH=CR'R'' 790-840	w-m vw-m m + s s m-s, broad s s	=C-H stretch C=C stretch =C-H bend =C-H bend =C-H bend =C-H bend	Esters	aliphatic 1160-1210 acetates ~1240 aromatic 1250-1310 R-C(O)-O-R 1735-1750 C=C-C(O)-O-R or Ar-C(O)-O-R 1715-1730 R-C(O)-O-Ar 1760-1790	s-vs s s s	O=C-O-C stretch C=O stretch C=O stretch C=O stretch
Alkynes	R-C≡C-H 3265-3335 2100-2140 610-700 R-C≡C-R' 2190-2260	s, sharp m s, broad vw-w	≡C-H stretch C≡C stretch ≡C-H bend C≡C stretch	Acyl Chlorides	R-C(O)-Cl 1785-1815 Ar-C(O)-Cl 1770-1800	s s	C=O stretch C=O stretch
Alkyl halides	R-F 1000-1350 R-Cl 750-850 R-Br 500-680 R-I 200-500	vs s s s	C-F stretch C-Cl stretch C-Br stretch C-I stretch	Anhydrides	R-C(O)-O-C(O)-R ~1750 + ~1815 Ar-C(O)-O-C(O)-Ar ~1720 + ~1775 (both two bands)	s,s s,s	C=O symmetric & asym. stretch
Alcohols	3300-3400 C=C-CH ₂ -OH 1035-1050 R-CH ₂ -OH (1°) or C=C-CH(R)-OH 1050-1085 RR'CH-OH (2°) or C=C-CRR'-OH 1085-1125 RR'R''C-OH (3°) 1125-1205 Ar-O-H 1180-1260	s, broad m-s m-s m-s m-s m-s	O-H stretch C-O stretch C-O stretch C-O stretch C-O stretch C-O stretch	Nitriles	R-C≡N 2240-2260 C≡C≡N or Ar-C≡N 2220-2240	m-s s	C≡N stretch C≡N stretch
Ethers	R-O-R' 1085-1150 Ar-O-R 1020-1075 and 1200-1275 (two band)	s m-s	C-O-C stretch =C-O-C sym. & asym. stretch	Amines	R-NH ₂ ~3400 + ~3500 (two bands) 1580-1650 RR'N-H 3310-33350	w w-m w	N-H symmetric & asym. stretch N-H bend N-H stretch
Aldehydes	2700-2725 R-CH=O 1720-1740 C=C-CH=O or Ar-CH=O 1685-1710	m s s	H-C=O stretch C=O stretch C=O stretch	Amides	R-C(O)-NH ₂ 3200-3400 and 3400-3500 (two bands) 1650-1690 1590-1655 R-C(O)-NH-R 3400-3500 1640-1690 1510-1560 R-C(O)-NR'R'' 1630-1680	w-m s, broad m-s w-m s, broad m-s m-s	N-H symmetric & asym. stretch C=O stretch N-H bend N-H stretch C=O stretch N-H bend C=O stretch
Ketones	RR'C=O 1710-1720 C=C-C(O)-R 1665-1685 Ar-C(O)-R 1675-1695 four member cyclic 1770-1780 five member cyclic 1740-1755 six member cyclic 1710-1720	s s s s s s	C=O stretch C=O stretch C=O stretch C=O stretch C=O stretch C=O stretch	Nitro Compounds	R-NO ₂ ~1550 and ~1370 C=C-NO ₂ or Ar-NO ₂ ~1525 and ~1335 (both two bands)	s s s s	N-O symmetric & asym. stretch N-O symmetric & asym. stretch
				Aromatic Compounds	3010-3100 1450-1600 (two to four bands) monosubstituted 730-770 and 690-710 (two bands) <i>o</i> -disubstituted 735-770 <i>m</i> -disubstituted 750-810 and 690-710 <i>p</i> -disubstituted 810-840	m m-s sharp s s s s s	Ar C-H stretch ring C=C stretch C-H bend C-H bend C-H bend C-H bend C-H bend C-H bend

Intensity abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Standard chemical shift value (ppm from TMS)

Alkane	C-1	C-2	C-3	C-4	C-5
Methane	-2.5				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2	13.4	
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Isobutene	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Neopentane	31.7	28.1			
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH ₃)	

¹³C chemical shifts for some linear and branched-chain alkanes

Olefinic carbons	
Substituent carbon C	Correction
α	+10.6
β	+7.2
γ	-1.5
α'	-7.9
B'	-1.8
γ'	-1.5
z (cis)	-1.1

Increments* (ppm) for substituents Y on alkanes

Substituent Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+9	+6	+10	+8	-2
HC=CH ₂	+20		+6		-0.5
C $\equiv$ CH	+4.5		+5.5	+2	-3.5
COOH	+21	+16	+3	+2	-2
COO ⁻	+25	+20	+5	+3	-2
COOR	+20	+17	+3	+2	-2
COCl	+33	+28		+2	
CONH ₂	+22		+2.5		-0.5
COR	+30	+24	+1	+1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+9	+7	-2
OH	+48	+41	+10	+8	-5
OR	+58	+51	+8	+5	-4
OCOR	+51	+45	+6	+5	-3
NH ₂	+29	+24	+11	+10	-5
NH ₃ ⁺	+26	+24	+8	+6	-5
NHR	+37	+31	+8	+6	-4
NR ₂	+42		+6		-3
NH ₃ ⁺	+31		+5		-7
NO ₂	+63	+57	+4	+4	
CN	+4	+1	+3	+3	-3
SH	+11	+11	+12	+11	-4
SR	+20		+7		-3
F	+68	+63	+9	+6	-4
Cl	+31	+32	+11	+10	-4
Br	+20	+25	+11	+10	-3
I	-6	+4	+11	+12	-1

**Increments in the shifts of the aromatic carbon atoms of monosubstituted benzenes
(ppm from benzene at 128.5 ppm)**

Substituent	C-1	C-2 (<i>ortho</i>)	C-3 (<i>meta</i>)	C-4 (<i>para</i>)
H	0.0	0.0	0.0	0.0
CH ₃	+9.3	+0.7	-0.1	-2.9
CH ₃ CH ₂	+15.6	-0.5	0.0	-2.6
CH(CH ₃) ₂	+20.1	-2.0	0.0	-2.5
HC=CH ₂	+9.1	-2.4	+0.2	-0.5
C ₆ H ₅	+12.1	-1.8	-0.1	-1.6
F	+35.1	-14.3	+0.9	-4.5
Cl	+6.4	+0.2	+1.0	-2.0
Br	-5.4	+3.4	+2.2	-1.0
I	-32.2	+9.9	+2.6	-7.3
OH	+26.6	-12.7	+1.6	-7.3
OCH ₃	+31.4	-14.4	+1.0	-7.7
CHO	+8.2	+1.2	+0.6	+5.8
COCH ₃	+7.8	-0.4	-0.4	+2.8
COOH	+2.9	+1.3	+0.4	+4.3
CN	-16.0	+3.6	+0.6	+4.3
NO ₂	+19.6	-5.3	+0.9	+6.0
NH ₂	+19.2	-12.4	+1.3	-9.5
NHCOCH ₃	+11.1	-9.9	+0.2	-5.6
COOCH ₃	+2.0	+1.2	-0.1	+4.8
